Effect of Nanoparticles on the Wetting of Different Solid Surfaces

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Thesis submitted

By

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In partial fulfillment as a requirements for the degree of Bachelor of Technology

In

Chemical Engineering

Under the guidance of

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DEPARTMENT OF CHEMICAL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA

2010-2011

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA 2011

CERTIFICATE

This is to certify that the thesis entitled, **"Effect of nanoparticles on the wetting of different solid surfaces"** submitted by **Miss Savitri Hasda** in partial fulfillment of the requirements of the award of Bachelor of Technology Degree in Chemical Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

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ACKNOWLEDGEMENT

I wish to express my deep sense of gratitude and indebtedness to Prof. Santanu Paria, department of Chemical Engineering, N I T Rourkela for introducing the topic and for their inspiring guidance, constructive criticism and valuable suggestion throughout this project work.

I want to acknowledge the support and encouragement of Mr Rajib Ghosh Chaudhuri in the lab work.

I owe a depth of gratitude to Prof K. C. Biswal, H.O.D. of Chemical Engineering department, National Institute of Technology, Rourkela, and all other faculties for all the facilities provided during the course of my tenure.

I am also thankful to research scholars in Department of Chemical Engineering for helping me out in different ways.

20th June 2011 (SAVITRI HASDA)

Contents

Abstract

The wetting of solids by liquid is gaining a lot of importance as it is connected to physical chemistry (wettability) to statistical physics (wetting transition) and long-range forces (van der Waals, double layer) to fluid dynamics. The present study mainly focused on the effect of nanoparticles on the wetting of different solid surfaces, as nanoparticles are gaining importance because of their wide applications in various field like pharmaceutical, biomedical and electronics. The effect of two different nanoparticles hydrophobic (sulfur) and hydrophilic (TiO_2) on both the hydrophilic (glass) and hydrophobic (PTFE) surfaces have been studied. The sulfur nanoparticles were prepared by acid catalyzed precipitation reaction from sodium thiosulphate, whereas TiO_2 is prepared by hydrolysis of trititanium (IV) butaoxide (TBOT). It is observed the use of nanoparticles enhanced the wetting process as compared to the base liquids without nanoparticles. The effect of reactant concentration on the particles size of both particles is initially studied and the results shows with increasing concentration the particles size increases in both the cases. Then the effect of particles size on the wetting of glass and PTFE surfaces were studied by measuring surface tension and contact angle. In the presence of the sulfur particles the wetting property of the both surfaces increases whereas, due to the presence of TiO_2 particles the wetting property increases for PTFE surface but the wetting property decreases for the glass surface. The extent of measurement of wetting process was done by calculating work of adhesion, Hamaker constant, and wetting free energy for both the surfaces in the presence of both particles.

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Nomenclature

CMC	-	Critical micelle concentration
AKD	-	Alkylketene dimmer
SA	-	Sodium acetate
MEGA-10	-	n-decanoyl-n-methylgluamine
SDS	-	Sodium dodecyl sulfate
HTAB	-	Hexa decyltrimethyl ammonium bromide
CTAB	-	Cetyltrimethyl ammonium bromide
PTFE	-	Polytetrafluoroethylene
CPyB	-	Cetyl Pyridinium bromide
SDDS	-	2-Sulfamoyl-4, 4-diaminodiphenyl sulfone
SNP	-	Silicon nanoparticle
IO	-	Indium oxide
DEG	-	Diethylene glycol
DI	-	De-ionized
TBOT	-	Trititanium(IV) butaoxide
DLS	-	Dynamic light scattering
TX-100	-	Triton X-100

Chapter 1

INTRODUCTION

1. Introduction

1.1 Importance of wetting

From the last few decades wetting of solid surfaces has been a topic of immense interest with ranges of applications. It is the phenomena of ability of a liquid to maintain contact with the solid surface, resulting from intermolecular interaction when the two phases are brought together. A large number of industrial fields such as solid-liquid separation in wetting media, surface cleaning, dust abatement coating, adhesion, pritining and detergency demand a basic understanding of the wetting process, and the parameters affecting process. Various phenomena like van der Waals interaction, interfacial free energy, spreading and capillary flow can be easily explained if we know the wetting and dewetting properties of the surfaces.

1.2 Wetting of a solid surface

Wettability of a solid surface is quantitatively measured in terms of contact angle. The contact angle is the angle at which the liquid-vapor interface meets solid-surface interface. As the tendency of a liquid drop is to spread out over a flat, solid surface increases, contact angle decreases. Thus, the contact angle provides a direct measurement of wettability. A contact angle less than 90° usually indicate wetting of the surface is very favorable, and the liquid will spread over a large area of the surface. Contact angles greater than 90° generally mean that wetting of the surface is unfavorable so the fluid will minimize contact with the surface and form compact liquid droplet.

The solid surfaces are broadly classified as hydrophobic or hydrophilic depending upon the extent to which the wetting of the surface is facilitated. Hydrophilic surface as the name itself implies, means surfaces having affinity to water. Since the contact angle formed is less than 90°, the exposed area of liquid to air is less. Water spreads very well on these surfaces. Glass is an example of this type of surfaces. On the other hand, on hydrophobic surfaces, water does not spread well. The water drops formed on these surfaces have higher surface energy forming the contact angle always more than 90°.

1.3 Contact angle

Contact angle measurements are widely used for the evaluation of macroscopic surface characteristics such as wettability, hydrophobicity, adhesion, and the surface tension of solids.

Theoretical as well as practical reasons lead to extending such measurements to the nanometre scale. For instance, the contact angle of nano scale droplets on a given solid is expected to differ from the one measured at the macroscopic scale because of long range solid-liquid interactions and unsaturated intermolecular interactions at the three-phase contact line.

1.3.1 Angles and energies:Youngs equation

The theoretical description of contact arises from the consideration of a thermodynamic equilibrium between the three phases: the liquid, solid and the gas/vapor phases. It is convenient to frame the discussion in terms of the interfacial energies.

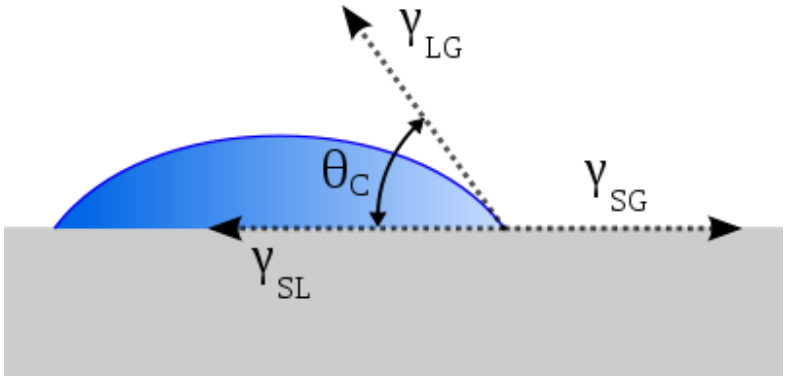

Figure 1.1 A contact angle of a liquid sample

According to Young equation

$$\gamma SG = \gamma SL + \gamma cos\theta \quad (1)$$

Where γ_{SG} denote solid-vapor interfacial energy, the γ_{SL} denotes solid-liquid interfacial energy and the liquid-vapor energy is simply denoted by γ and θ is the equilibrium contact angle. The Young equations assumes a perfectly flat surface, and in many cases a deviation in the equilibrium contact angle from the contact angle is causes by surface roughness and impurities predicted by Young's equation.

1.3.2 Special features of wetting

Above equation gives $cos\theta$ in terms of interfacial energies. The special case

$$\gamma = \gamma SG - \gamma SL \quad (2)$$

leads to cosθ=1 or cosθ=0 complete wetting. In case of partial wetting wetted surface is delimited by certain contact line.

1.3.3. Types of wetting

In general term wetting can be categorized in the following ways:

1.3.3.1 Adhesional wetting: Adhesional wetting is a process in which an adhesional joint is formed between two phases. The work of adhesional per unit area can be defined as, the work done on the system when two condensed phases forming an interface of unit area are separated reversibly forming unit area of each of the interfaces.

1.3.3.2 Spreading wetting: It is the process in which liquid drops spreads over a solid or liquid substrate. When a liquid is placed on the solid or liquid surfaces, both previously in contact with fluid phase, will tend to spread on the surface if the spreading parameter (S), which measure the difference between surface energy(per unit area) of substrate when dry and wet.

$$S = [E_{substrate}]_{dry} - [E_{substrate,}]_{wet} \quad (3)$$

$$S = \gamma_{SG} - (\gamma_{SL} + \gamma_{LV}) \quad (4)$$

Where γ_{SG}, γ_{SL} and γ_{LV} are the surface tension on solid-vapor, solid-liquid and liquid-vapor interface.

S>0: Total wetting.

If the spreading parameter is positive, the liquid spread completely to lower its surface energy.

S<0: Partially wetting.

If the spreading parameter is negative, the drop does not spread, instead forming a spherical cap at equilibrium resting on the substrate.

1.3.3.3 Immersional wetting: It is a process in which a solid or liquid is covered with a liquid, initially in contact with a gas or liquid, without changing the area of interface.

1.4 Effect of nanoparticles on wetting of solid surfaces

When nanoparticles were added to the base liquid, a distinct “stick-slip” behavior occurred. Increased nanoparticles concentration increased the “stick-slip” behavior. Smaller size

nanoparticles lead to larger changes in contact angle at the same mass concentration. These contribute to understanding the role of functionalized nanoparticles in surface wettability.

The contact angle of the surfaces decrease with increasing surface coverage; that is hydrophobic surface was changed to hydrophilic surface by adding nanoparticles. This effect is due to a decreased in the hydrophobic surface area on the surface.

1.5 Surfactants effect on the wetting of a solid surfaces

The wetting of surfaces by surfactant solutions is very important in surface and interface science, owing to the fact that many industrial processes and daily life applications are impossible to consider without wetting. In the wetting process, adsorption of surfactant at the solid- liquid interface and surface tension at the air-liquid interface plays an important role. Because hydrophobic surfaces have very low surface energies, wetting with a polar solvent is difficult and can be enhanced using surfactants. Surfactants having low surface tension values at the critical micelle concentration (CMC) and low solid-water interfacial tension upon the adsorption of surfactants always show better wetting properties. In view of the widespread applications of wetting phenomena, many researchers have studied the wettability of different types of hydrophilic and hydrophobic surfaces by different single surfactants, mixed surfactant systems, and additives. In mixed surfactant systems, mixtures of similar cationic and non-ionic and dissimilar mixtures of both cationic and non-ionic surfactants have been studied. The effects of different additives such as alcohols and electrolytes have also been studied thoroughly (Biswal and Paria, 2011).

Chapter 2

LITERATURE REVIEW

2.1 Introduction

The wetting and dewetting of solid surface by a liquid is a comprehensive problem whose solution involves a variety of discipline, such as physical chemistry (van der Waals interaction and double layer), surface chemistry (surface structure and interfacial free energy), statistical mechanics (pinning of contact line and transition of wetting morphology) and fluid dynamics (spreading and capillary flow). Despite the fact that it has long been recognized that surface heterogeneity will also play an important role in determining the thermodynamics and kinetics of wetting or dewetting, the surface was usually considered as homogeneous and perfectly flat in classical studies. Only under this assumption, a meaningful contact angle can be measured for each liquid–solid interface, and be subsequently used to fully describe the wettability of a solid surface.

2.2 Effect of surfactant on wetting

Surfaces with contact angle larger than 150° are called as super-hydrophobic or water-repellent. Theses surfaces are important in practical applications such as glass covers for solar cells, windshields of automobiles, roofing, eyeglasses, and generally anywhere where reducing wetting or adhesion is desirable.

Three main factors that control the wetting of a solid are: surface roughness, surface energy and homogeneity. Surfaces those have low surface energy and high degree of roughness show super-hydrophobicity. By lowering the surface energy the highest contact angle for water on smooth surface is to be noted as 120°. Beyond this angle, the surface roughness which is produced by a fractal structure, for example, is a dominating factor in increasing the contact angle. By roughening the low surface energy materials through chemical treatment we can obtain contact angle more than 170° for water. The cleanliness of the super-hydrophobic surfaces and the purity of the water are important factors in wetting of a solid surface. A small amount of surfactant on the surface or in the test liquid could significantly change the wettability in practical applications. Figure 2.1 show the contact angle hysteresis, which is defined as the difference between advancing and receding contact angles, which is first increases and then decreases over time as prickly structures form. This behavior shows the transition from the Wenzel wetting regime to a composite Cassie regime.

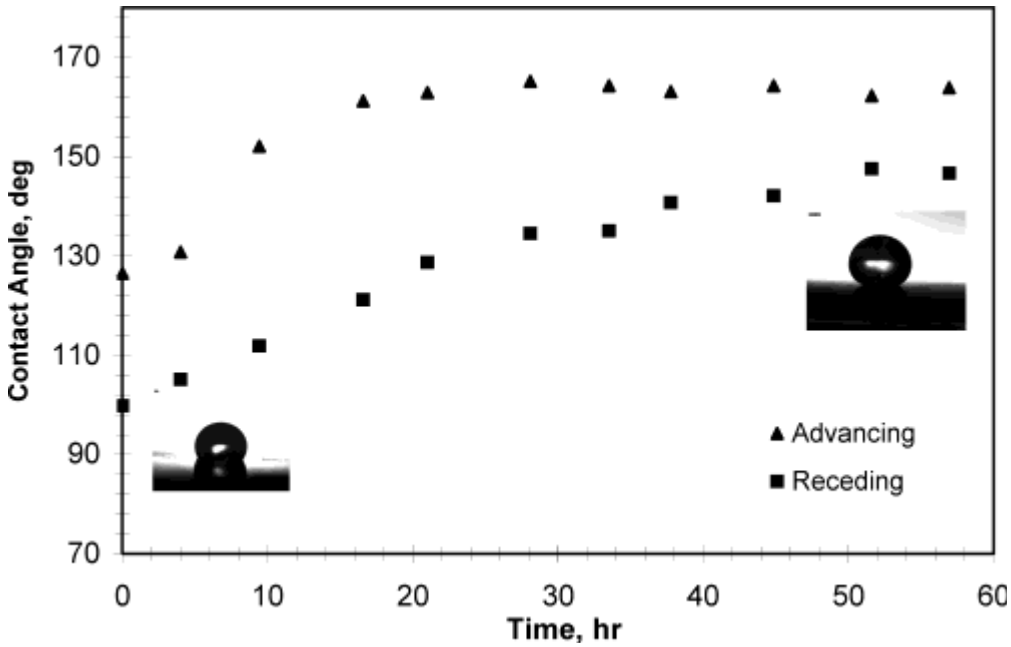

Figure 2.1 Advancing and receding contact angle change for distilled water on alkylketene dime (AKD) surfaces over time.

Both advancing and receding contact angles increase with time to reach the final values of about 164 and 147°, respectively. The images of the two drops show the water drop on a relatively smooth AKD surface (left image) with a contact angle of about 126° and on a super-hydrophobic AKD surface (right image) with a contact angle of about 164°.(Mohammandi,R. et al,2004)

Figure 2.2 shows the changes in surface tension and advancing contact angle with concentration for the surfactants in water. From figure 2.2a it can be seen that with increase in the concentration of the surfactant in water, surface tension decrease and then starts to level off at the CMC for SDS (7−8 mmol), HTAB (0.8−0.9 mmol), and MEGA 10 (6−7 mmol). This type of behavior is not observed for SA. To some extent the behavior of the advancing contact angle versus concentration for all of the surfactant solutions is similar to that of surface tension (Figure 2b); that is, it decreases with concentrations. As the result of different interaction of the surfactant with alkylketene dimer (AKD) surface, each surfactant solution shows a different behavior in the advancing contact angle at high concentrations (e.g., near the CMC) possibly.

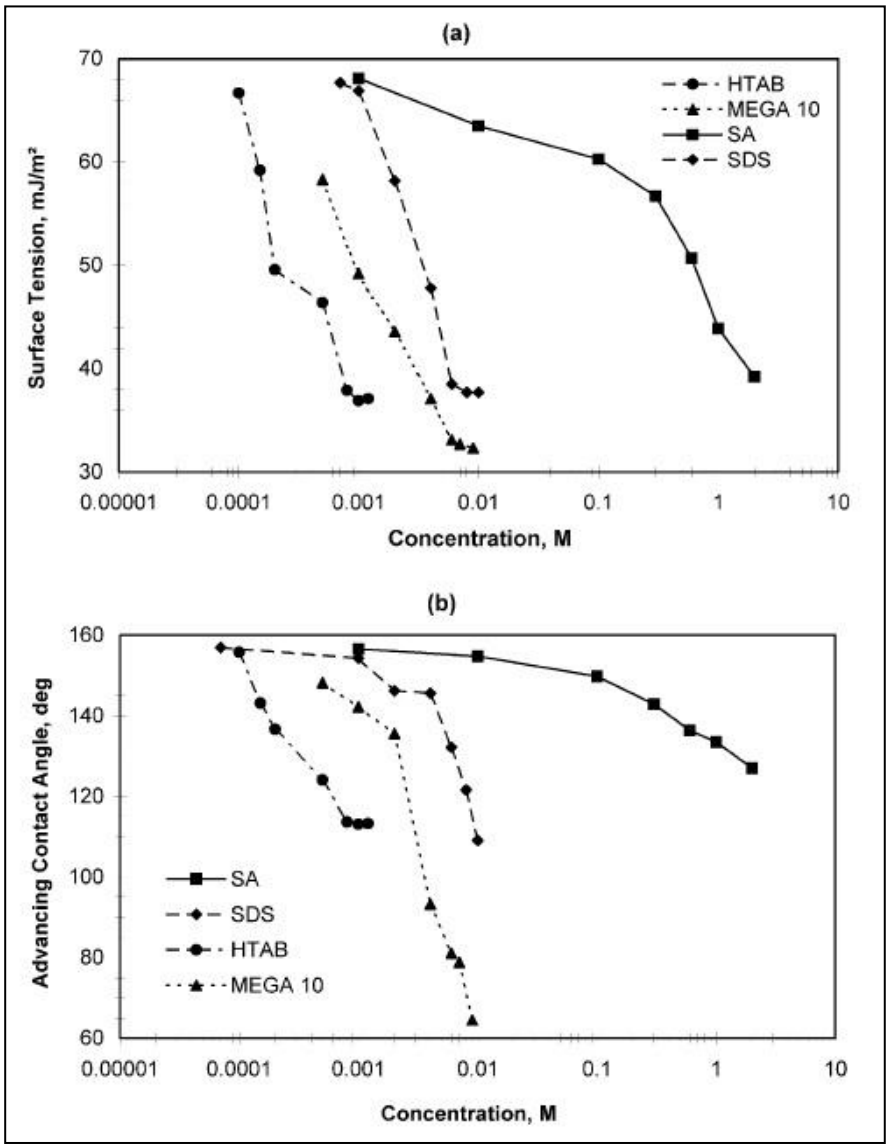

Figure 2.2. (a) Surface tension versus concentration in water for SA, SDS, HTAB, and MEGA 10. The surface tension decreases with concentration and levels off at the CMC for SDS (9−10mmol), HTAB (0.8−0.9mmol), and MEGA 10 (7−8mmol). (b) Advancing contact angle versus concentration in water for the surfactants as mentioned earlier. (Mohammandi, R. et al, 2004.)

2.2.1 Effect of pure surfactant aqueous solution on wetting

The wetting and dewetting behavior of pure surfactant aqueous solution on the substrate is not only dependent on the interaction, but also limited by the maximum equilibrium concentration of surfactant at the interface.

Advancing and receding contact angles for various concentrations of four surfactant (SA, SDS, HTAB, and MEGA 10) solutions in water are shown in Figure 2.3a−d. These graphs show that for all aqueous solutions of the surfactants, both advancing and receding contact

angles decrease with increase in concentration of surfactant in water. However, even at very high concentrations solutions corresponding to significant reduction in surface tension for water (e.g., 50%), the surface remains very hydrophobic (except MEGA 10 at concentrations very close to the CMC (7−8mmol)). From Figure2.3, one can also observe that the contact angle hysteresis decreases with concentration for SA, HTAB, and MEGA 10 solutions. The addition of a small amount of nonionic surfactant (e.g., 0.6mmol MEGA 10) seemingly improves the sliding behavior of a drop on an inclined surface (lowering contact angle hysteresis), without much change in the observed advancing contact angle (see Figure 2.3d).

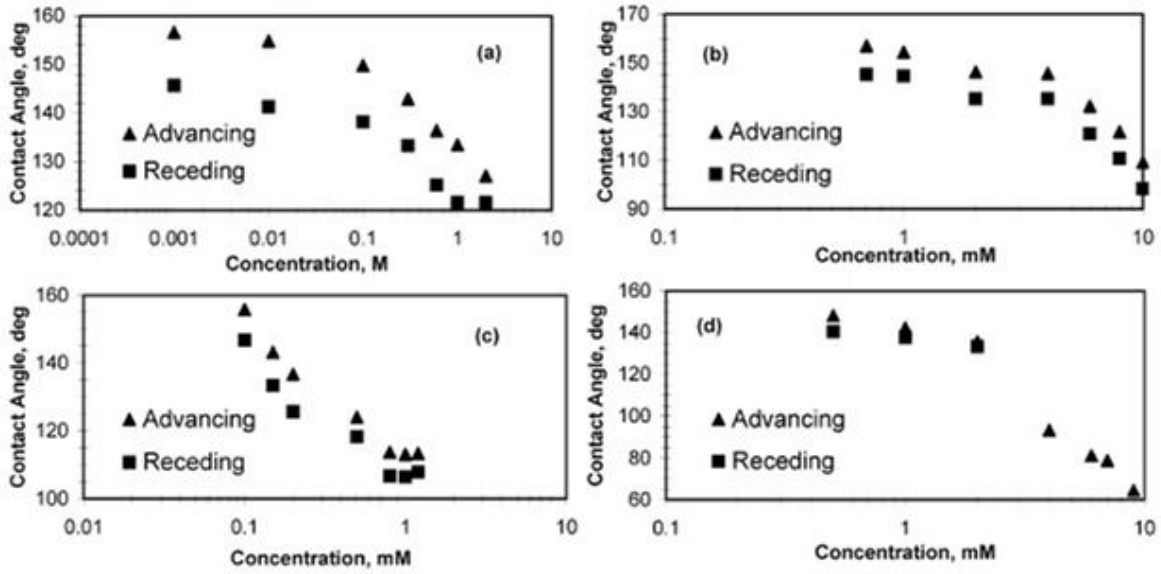

Figure 2.3 Advancing and receding contact angles versus concentration for four surfactant solutions. (a) SA, (b) SDS, (c) HTAB and (d) MEGA 10. (Mohammandi, R. et al, 2004).

The contact angles of all four surfactant solutions decrease by increasing the concentration of the surfactants in water, but even at a high concentration of surfactants (representing about 50% reduction in surface tension), the surfaces remain hydrophobic.

Table 2.1. Average surface tension and contact angles of pure liquids on the super-hydrophobic AKD surfaces. (Mohammadi, R. et al, 2004)

Liquid	Average surface tension (mJ/m^2)	Average contact angle (deg)
Water	72.2	160.3 ± 0.65
Ethylene glycol	47.0	133.3 ± 0.43
1-bromonaphthalene	44.3	<20
Dibenzylamine	40.8	<10
Ethylcinnamate	37.2	<10
cis-decalin	32.3	0
Hexadecane	27.0	0

Figure 2.4 shows the surface tension versus advancing contact angle for different surfactant solutions and pure liquids. Although at high concentration the surface tensions of surfactant solutions are close to those of some of the pure liquids (see the region enclosed in the dotted rectangle in Figure2.4) the contact angles are very different.

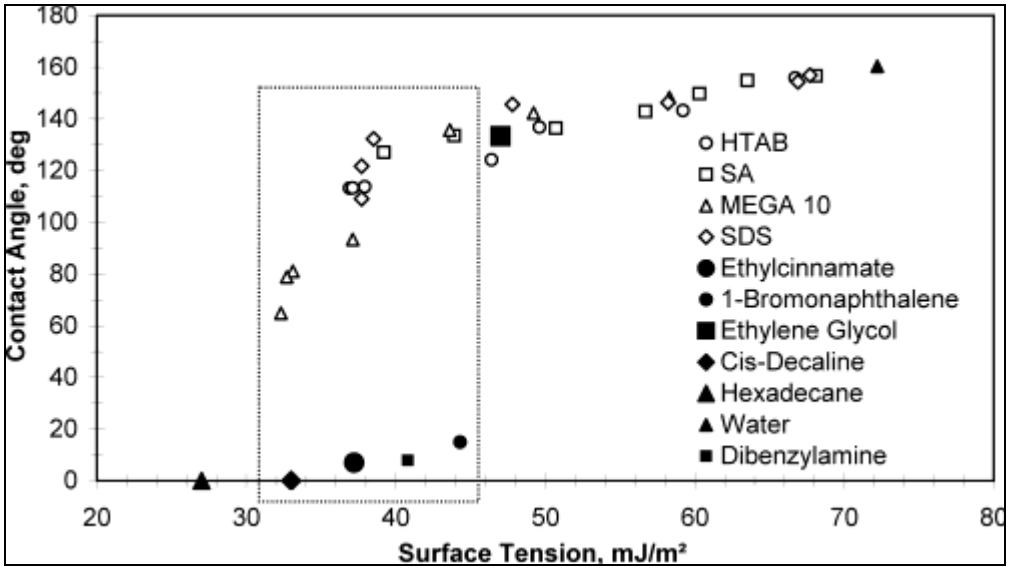

Figure 2. 4 Surface tension versus contact angle for different surfactant system and pure liquids. (Mohammandi, R. et al, 2004).

The dotted rectangles highlight the liquids (pure liquids shown with solid symbols and aqueous solutions of surfactants shown with open symbols) with close surface tensions having very different advancing contact angles.

On the smooth AKD surface, the contact angle of a liquid with a specific surface tension can be below or above 90°. Pure liquids with contact angles of below 90° on smooth AKD surface show contact angles of less than 20° on super-hydrophobic AKD surface. Pure liquids with contact angles on smooth AKD surfaces of above 90° (e.g., ethylene glycol or water) show contact angles higher than 90° with rough AKD, and the Wenzel or Cassie mode is valid . Surfactant solutions that have surface tensions similar to those of pure liquids (with expected intrinsic contact angles of less than 90° on smooth AKD) show contact angles generally above 90° on rough AKD surfaces. Therefore, the wetting behavior (characterized by the contact angle) of surfactant solutions is not similar to what was seen for pure liquids.

High contact angles, result for surfactant solutions when compared to pure liquids with similar low surface tensions. In comparing the contact angles of surfactant solutions with those of pure liquids it should be noted that the adsorption of the surfactants to the surface might change the solid surface energy and, hence, influence the observed contact angle to a limited degree.

2.2.2 Effect of mixed surfactant

Properties of different surfactant or the same type were mixed together and their properties were studied. The role of a mixed surfactant system in enhancing wetting properties was investigated. Mixed surfactant system usually has a critical micelle concentration which may be greater than or less than that of individual ones depending upon the interaction between individual surfactant molecules, the effects being named as antagonism or synergism respectively. In the cases where a lower CMC value is achieved, a more economical way of changing surface properties is provided. The mixed surfactant system is unexplored area as compared to that of single surfactant.

Mixtures of two surfactants system showed deviation from the linear dependence between the contact angle and mixture composition, however, no synergism in the wettability was observed. If a mixture of ionic and non-ionic surfactants is added to water, a synergism in the wettability of low-energetic hydrophobic solids should be expected (Rosen, 2004; Gharibi et al. 2000; Li et al., 1998). The variation of contact angle with mole fraction of a particular

surfactant in a mixture of two cationic surfactants is given by Szymczyk et al. (2006) which is presented in figure-2. 5

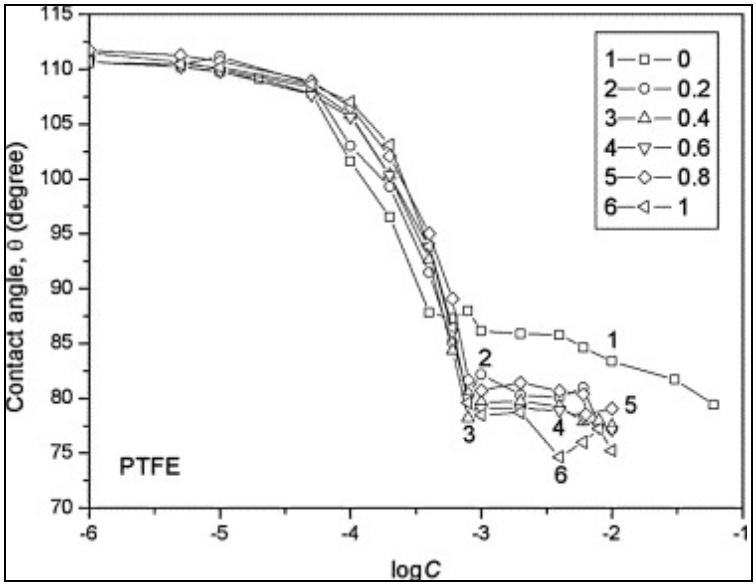

Fig-2.5The relationship between the contact angle, θ, and log$C$ (where C is the total concentration of the mixture) for different values of the monomer mole fraction of CTAB, α, in CPyB and CTAB mixture (for PTFE). (Szymczyk et al., 2006)

Szymczyk and Janczuk (2006) also studied the behaviour of a cationic-nonionic mixture for which the trend as given in figure-2.6 was followed.

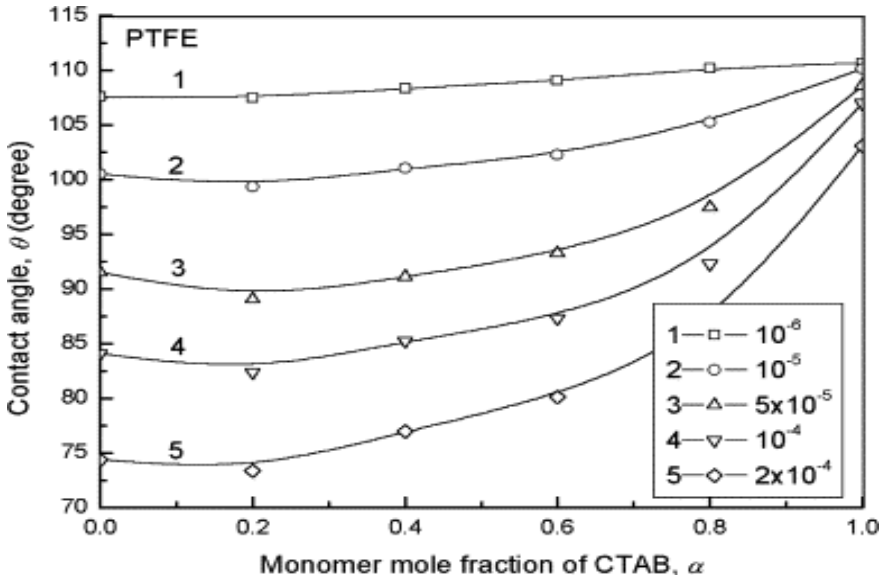

Fig-.2.6. The relationship between the contact angle, θ, and monomer mole fraction of CTAB, α, in TX100 and CTAB mixture (for PTFE) at constant total mixture concentration, C, equal to 10^{-6} (curve 1), 10^{-5} (curve 2), 5×10^{-5} (curve 3) 10^{-4} (curve 4) and 2×10^{-4} M (curve 5). (Szymczyk and Janczuk, 2006).

Zdziennicka et al. (2003) studied the wettability of polytetrafluoroethylene by aqueous solutions of two anionic surfactant mixtures and the variation of contact angle with logC was plotted for different ratios.

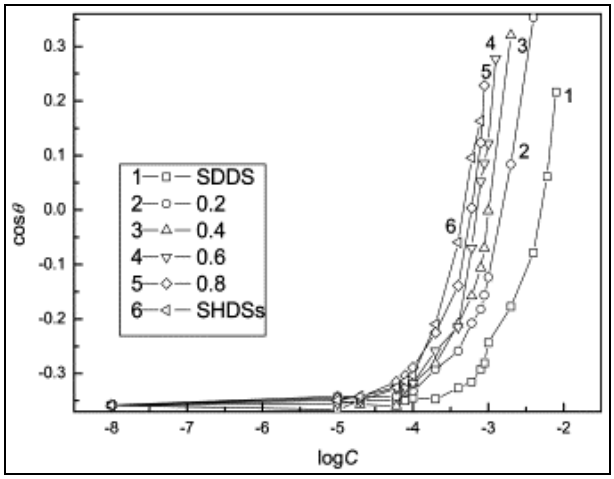

Fig-2.7 the relationship between cosθ (θ—contact angle) and logarithm *C* for different values of the mole fraction (α) of SHDSs in SDDS+SHDSs mixture (Zdziennicka et al., 2003).

2.3 Effect of surfactant with additive

The presence of a small amount of anionic and cationic surfactants on the super-hydrophobic surface or in the test liquid decreases the hydrophobicity of the surface. The advancing contact angle of solutions on the surface decreases from 164 to about 110° depending on the structure and concentration of the surfactants in the solution.

In many industrial applications additives are used along with surfactants to improve wetting property. Presence of additives greatly influences various wetting parameters thus providing a more effective way of achieving the desired wettability. Mostly the additives used include alcohols and electrolytes.

2.3.1 Effect of Alcohols

Great deal of research as done by Rosen (2004), Zana (1995), Forland et al. (1994), Forland et al. (1998), Attwood et al. (1994), Zana et al. (1981), Rao and Ruckenstein (1986), Castedo et al. (1997) and Leung and Shah (1986) are presented on the solution behavior of alcohol and surfactant mixture in changing wetting behaviors. The variation of contact angle with concentration of alcohol was presented by Zdziennicka and Janczuk (2008), shown in figure-2.8

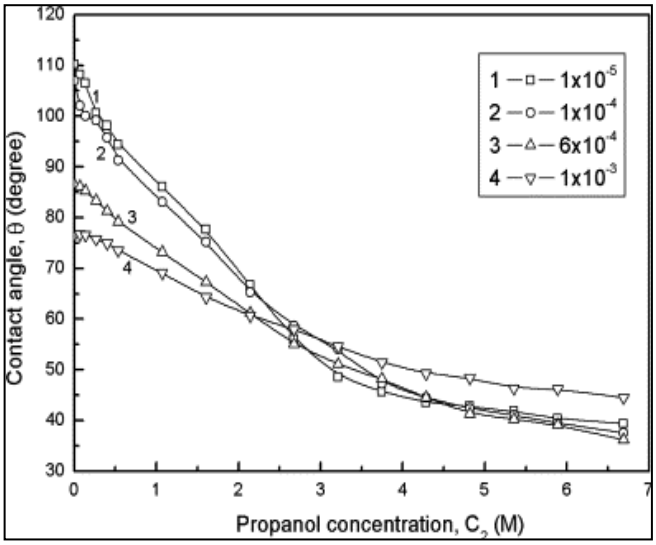

Figure 2.8 Dependence between the measured values of the contact angle (θ) and the propanol concentration. The constant values of CTAB equal to 1×10−5, 1×10−4, 6×10−4 and 1×10−3 M are correspond to the curve 1,2,3 and 4,respectively. (Zdziennicka and Janczuk, 2008).

The solution property as observed by alcohol surfactant mixture as given by Tomi et al. 2009 is presented in figure-2. 9.

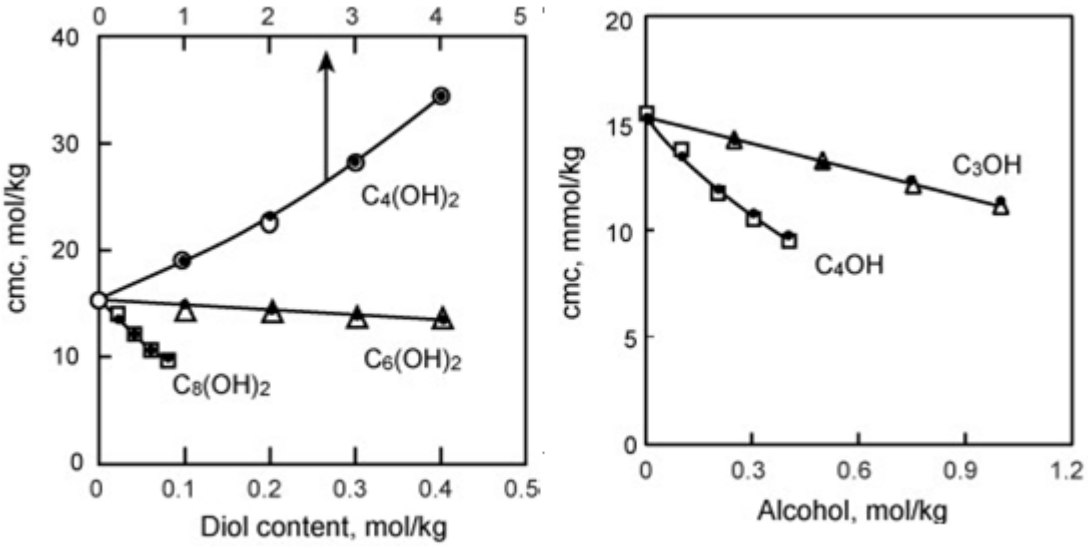

Figure-2.9 Dependence of cmc of DTAB solutions on alcohol content. Open marks denote the experimental results and solid marks denote the calculated values (Tomi et al. 2009)

2.3.2 Effect of electrolytes

The application of electrolytes as additives has been also studied recently. When we add electrolyte to a particular ionic surfactant solution it has been observed that surface tension and contact angle values are reduced because the presence of electrolyte decrease the repulsion between the head groups. Thus the CMC value is decreased.

So the addition of electrolyte can give a more economical way of using the surfactants for decreasing the contact angle and altering the wetting property. (Chaudhuri and Paria, 2009)

The addition of small amounts of neutral electrolyte to solutions of ionic surfactants appears to increase the extent of solubilization of hydrocarbons that are solubilized in the inner core of the micelle and to decrease that of polar compounds that are solubilized in the outer portion of the layer (Klevens, 1950). The addition of neutral electrolyte to solutions of nonionic surfactants increases the extent of solubilization of hydrocarbons at a given temperature in those cases where electrolyte addition causes an increase in the aggregation number of the micelles. The order of increase in solubilization appears to be the same as that for depression of the cloud point (Section IIIB, below) (Saito, 1967): $K^+ > Na^+ > Li^+$; $Ca^{2+} > Al^{3+}$; $SO_4^{=} > Cl^-$. The effect of electrolyte addition on the solubilization of polar materials is not clear.

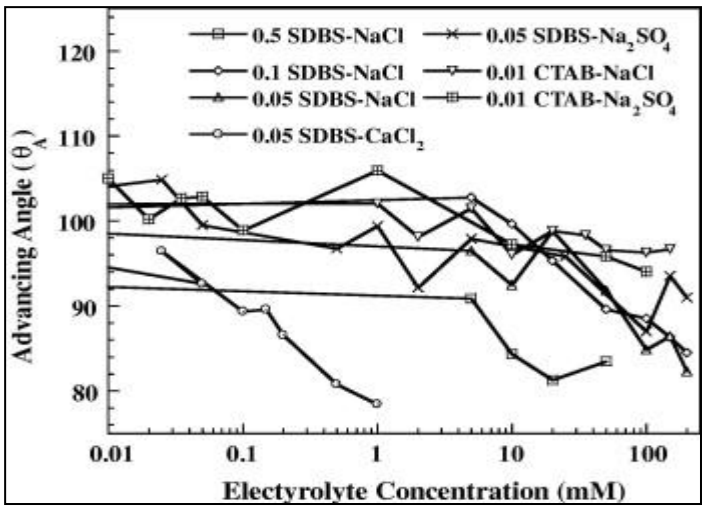

Figure 2.10. Plot of advancing contact angle for different electrolytes (NaCl, $CaCl_2$, Na2SO4) in the presence of CTAB and SDBS solution on PTFE surface. (Chaudhuri and Paria, 2009).

The above figure was obtained by Chaudhuri and Paria (2009) for effect of electrolyte on contact angle of pure surfactants. Variation of contact angle with concentration and valence of electrolyte is shown in the Figure 2.10. (Sunayana, 2010).

2.4 Effect of nanoparticles

Liquids containing nanoparticles exhibit different spreading or thinning behaviors on solids than liquids without nanoparticles. Various experiments and theoretical investigations have demonstrated that the spreading of nanofluids on solid surfaces is enhanced compared to the spreading of base fluids without nanoparticles. The wetting and spreading behavior of pure liquids over solid surfaces changes if liquids contain nano-sized spherical particles or surfactant micelles, globular proteins and macromolecules.

The contact angle of the surfaces decreased with increasing surface coverage; that is, the hydrophobic lignin surface was changed to hydrophilic by adding nanoparticles (NPs) (Figure 2.11). This effect is due to a decrease in the hydrophobic surface area on the surface. A similar behavior has been noted in an application where amine-functionalized particles have been applied on a surface.

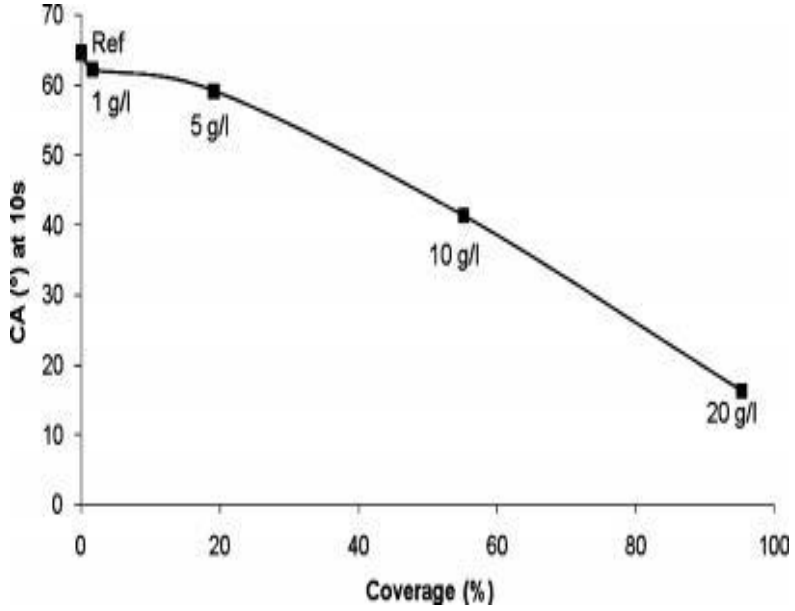

Figure 2.11. Contact angle data plotted against surface coverage (Dong, L.et al., 2010).

Figure 2.12 shows that the roughness of the surfaces first increased and then decreased with an increase in the surface coverage. It has been notice that the concentration can produce a fully covered rather smooth surface where the hydrophilic properties of the silicon nanoparticles (SNPs) dominate. That is the reason why the roughness increased with a few SNPs but then decreased when the surface was entirely covered by SNPs.

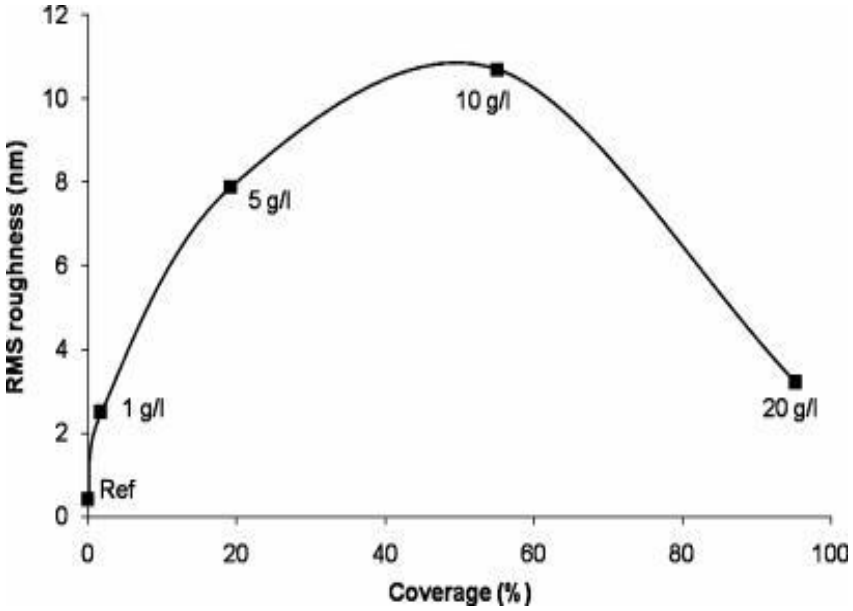

Figure 2.12 Roughness of the surface plotted against surface coverage (Dong, L.et al, 2010).

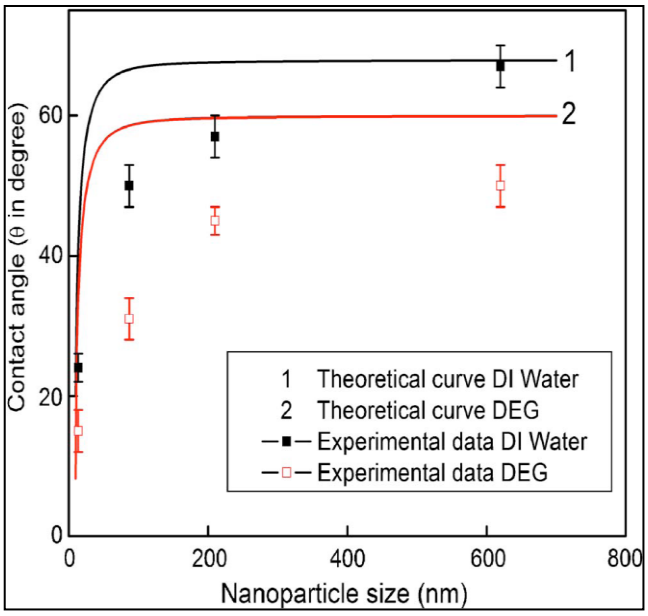

Figure 2.13. Color online variation of contact angle on Indium oxide (IO) nanoparticle sizes with de-ionized (DI) water solid squares and diethylene glycol (DEG) open squares droplets. The theoretical curves between contact angle and IO nanoparticle size for DI water and DEG droplets are also shown by solid lines 1 and 2, respectively, in the figure (Munshi et al, 2008).

The effects of the drop size, surface roughness, line tension dependence and heterogeneity of the solid surface on the contact angle have been reported in the literature. It has also been reported that the surface energy or the wettability of the surfaces changes with the surface treatment. Recently, there has been a very strong interest in the study of the contact angle on nanostructured materials. Fan *et al.2004* measured contact angle on a vertically aligned Si nanorod film. They observed that for as-deposited hydrophilic films, the hydrophilic nature increases with the film thickness while in the case of hydrofluoric acid treated hydrophobic films, the hydrophobic nature increases with the film thickness. They also observed that contact angles for both hydrophilic and hydrophobic surfaces experience a transition at a film thickness of about 500 nm. In other research work, Vafaei *et al.*2005 produced nanoparticles with sizes in the range of a few nanometers, and then investigated the effect of dispersed nanoparticles on the droplet contact angle. They observed that with an increase in the concentration, the measured contact angle increases, reaches a peak, and then decreases. The variations in contact angle as a function of concentration depend on the substrate material and particle size. For the same mass concentration, smaller size particles lead to larger changes in contact angle.

The measured contact angles for different samples are given in Table 2.2. The variation of contact angles on the nanoparticle size is shown in Figs. 2.13 for DI water and DEG droplets. It was observed that the contact angle increases with an increase in nanoparticle size and for a larger size of about 620 nm the contact angle value reaches 67°, which is close to the value of 68° observed for IO thin films.

Table 2.2. The variation of the contact angle and surface free energy of the IO nanoparticles with their sizes.

Nan particles size(nm)	**14±5**	**87±6**	**210±5**	**620±4**	**Thin film**
Contact angle with water (deg)	24	50	57	67	68
Contact angle with DEG (deg)	15	31	45	50	60
Surface free energy (10^{-3} N/m)	68.96	48.67	43.23	35	34.38
Disperse part (10^{-3} N/m)	7.86	12.28	9.26	11.71	6.67
Polar part (10^{-3} N/m)	61.09	36.39	33.97	23.28	27.7

The contact angle depends on the particle size and increases as the particle size increases from 14 to 620 nm. The surface energy may be one of the reasons for the variation between the contact angle and the nanoparticle size. For smaller sized nanoparticles, the surface to volume ratio increases, so the surface free energy increases, as shown in Table 2.2, which leads to a decrease in the contact angle. For larger sized particles, the opposite happens. There may be several other factors such as surface roughness and nanoparticles distribution on the substrate which can also control the contact angle. The difference in the areal density of the nanoparticles on the substrate for different nanoparticle sizes may cause the observed deviation in the theoretical and experimental values of contact angles, particularly for intermediate sized nanoparticles.

2.5 Research objective

In this project we have studied the wetting behaviour of surfaces. Our main objective in this study is to investigate the effect of nanoparticles on the wetting of the solid surfaces. Also we have attempted

- To correlate the surface tension and contact angle on wetting of solid surfaces.
- To measuring the wetting process from work of adhesion, Hamaker constant and wetting free energy for both surfaces in presence of both particles.
- Effect of surfactant on wetting of solid surfaces.
- Effect of reactant concentration on both the surfaces for the particles.

2.6 Organization of the thesis

In the thesis we have started with the brief introduction to contact angle on solid surfaces, wetting on solid surfaces and effect of nanoparticles on wetting of solid surfaces in chapter 1. Then we have given some literature review and the basis and the motivation of the project work in chapter 2. The material and the method section come in chapter 3 where all the material and their relevant properties have been specified in detail. The experimental methods are explained clearly. In chapter 4 result and discussion part is done and finally the conclusion of the project work is done in the last section.

Chapter 3

EXPERIMENTAL WORK

3.1 Materials

The chemicals sodium thiosulphate ($Na_2S_2O_35H_2O$) with 99.5% purity from Rankem (India), nitric acid (HNO_3) from Merck (India), tritinanium (IV) butaoxide (TBOT) from Sigma Aldrich (Germany) were used as it received without any further purification. Ultrapure water of 18.2 MX cm resistivity and pH 6.4-6.5 (Sartorius, Germany) was double distilled again and Teflon sheet are used for all the experiments. For particles size analyser, dynamic light scattering (DLS) using Malvern Zeta Size analyser from U.K (Nano ZS) is used.

3.2. Methods

3.2.1 Synthesis of particles

(a) TiO_2 particles synthesis

The stock $Ti(OC_4H_9)_4$ solution is prepared in anhydrous ethanol. TiO_2 particles were synthesis by the acid catalyzed sol-gel method. Inorganic HNO_3 was used as an acid. In this reaction at first $Ti(OC_4H_9)_4$ was hydrolyzed to $Ti(OH)_4$ in the presence of acid. Then $Ti(OH)_4$ was polymerized and condensed to TiO_2. After equilibration time 30mins, the sample was sonicated in a bath and particle size and contact angle were measured immediately after the sonication.

$$Ti(OC_4H_9)_4 + H_2O \longrightarrow Ti(OH)_4 + 4C_4H_9OH$$

$$Ti(OH)_4 \longrightarrow TiO_2 + H_2O$$

(b) Sulfur particles synthesis

The stock sodium thoisulphate were prepared by dissolving sodium thiosulphate in double distilled water and this reagent is filtered with 0.2 μ Nylon 6, 6 membrane filter paper from Pall life science, USA. When a dilute nitric acid (HNO_3) is added to sodium thiosulphate solution, a pale yellow precipitate of sulphur and sulphonic acid are formed according to the reaction.

$$Na_2S_2O_3 + 2HNO3 \rightarrow 2NaNO3 + H_2O + S \downarrow + SO2$$

$$SO_2 + H_2O \rightarrow H_2SO_3$$

As the $Na_2S_2O_3$ solution is diluted more and more, the precipitate takes longer and longer to form, 45 minutes equilibrium time is given for the completion of the reaction after mixing the reactant. After equilibration, the sample was sonicated in a bath and particle size and contact angle were measured immediately after the sonication.

3.2.2 Measurement of particle

Particle size measurement was carried out after bath sonication by dynamic light scattering (DLS) using Malvern Zeta Size analyser, U.K. (Nano ZS) with the help of cumulants fitting model and intensity distribution.

Figure 3.1 Dynamic Light Scattering using Malvern Zeta Size analyzer for particles size measurement.

3.2.3 Measurement of surface tension

A surface tensiometer, Data Physics, Germany (DCAT-11EC) was used for measuring surface tension. Platinum plate is used for surface tension measurement in Wilhelmy plate technique. Three readings for a particular solution were taken and for the final calculations, average of the three is taken.

To avoid the adsorption of particle on the plate it was cleaned properly with water and acetone and was also burned to ensure a clean surface. During the experiment, the temperature was maintained constant at a 25+0.5℃ with the help of a calculator.

Figure-3.2: Photograph of Surface Tensiometer

3.2.4 Measurement of contact angle

For measuring contact angle, contact angle meter, Data physics, Germany (OCA30) was used. Goniometric technique is used to calculate the contact angle. In Hamliton syringe solution is taken and forced out drop wise with droplets of a fixed volume which can be adjusted with the help of software. Pressing of the piston and movement of the base plate is also done by the instrument itself.

Figure-3.3: Photograph of video based optical contact angle meter

The Teflon sheets used for the experimental work were available in the form of rolled sheets due to which even a very small portion of a sheet was not found to be completely straight which could lead to deviation in contact angle results. So to avoid the problem, an arrangement of holding the sheet very tightly with the help of a base plate and four screws was made. (Sunayana, 2010). The Teflon sheet was washed with water, acetone and chromic acid to avoid the adsorption of particle on the surface. The plate was then dried under blowing hot air. The same procedure was repeated after the measurement of each reactant concentration.

Chapter 4

RESULT AND DISCUSSION

4.1 Effect of reactant concentration on the particles size

Figure 4.1 shows the effects of thiosulphate concentration on the sulfur particle. It is clear from the figure the with increasing thiosulphate concentration the particle size increases. Let us first consider the effect of reactant concentration on the particle size for a particular acid. The size of the particle is influenced by two factor (i) nucleation and (ii) particle growth. Nucleation process is instant and it's started as soon as the reactant is mixed with the acid. After that when there is a sufficient density of the nucleate molecule then the growth process is predominated over the nucleation process. But, the rate of reaction increases with increasing reactant concentration. According to LaMer (1948) rate of reaction = $k\,[T]^{1.5}\,[A]^{0.5}$, depend on both the concentration of thiosulphate and acid, where k is the reaction rate constant and [T] and [A] are the thiosulphate and acid concentration respectively. That means with increasing reactant concentration the density of nucleate particles also increase, therefore, after growth process ultimate particle size also increases for a particular acid. Finally, there is more collision between those particles (smaller particles gives more surface area on which collisions can occur) and due to coarsening those smaller particles lead to larger particles are stable by minimizing the overall energy of the system.

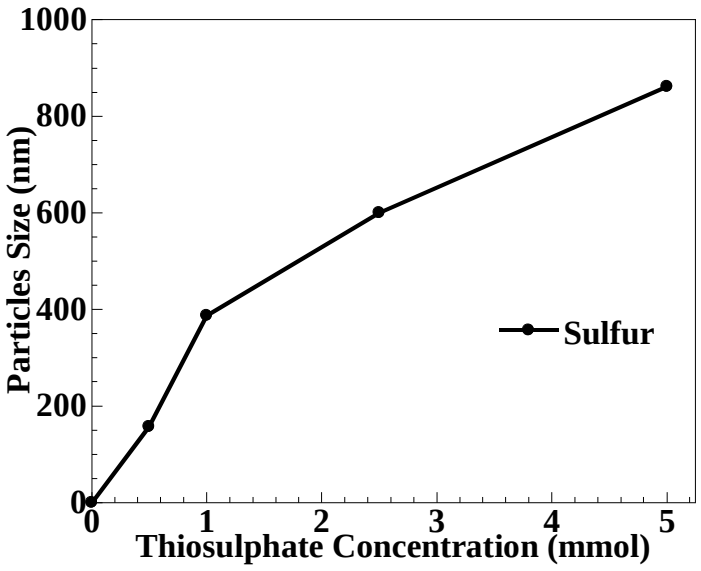

Figure 4.1 Effect of sodium thiosulphate concentration on the sulfur particle.

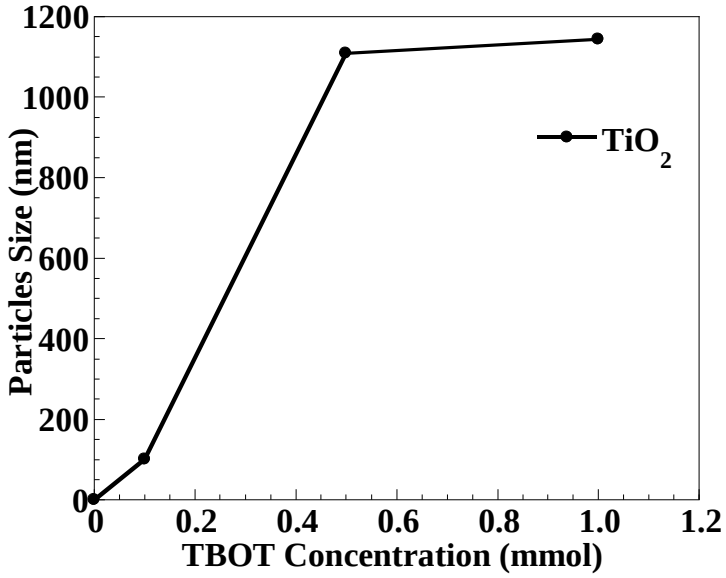

Figure 4.2 Effect of TBOT concentration (mmol) onTiO_2 particles.

As from the above result (figure 4.1), the effect of TBOT concentration on particle size follows the same trend. From figure 4.2, it is clear that at lower reactant concentration TiO_2 shows lowest particle size and when reactant concentration is high its shows a higher particle size.

4.2 Effect of particles on surface tension and contact angle

4.2.1 Effect on the glass surface

The surface tension of the liquid and the wettability of solid surfaces are properties that are closely related to contact angle. In a clean glass, water wet the glass surface and forming a low contact angle (49.4°) with the glass surface. In the figure 4.3 it is clearly shows that the particles solution will more effectively wet the glass surface and the surface tension and the contact angle will reduced. With increase in concentration, the contact angle and the surface tension decrease. At low concentration (0.5mmol) the surface tension and the contact angle values are 71.2nN/m and 49.5 (θ), respectively. At high concentration, say, 0.25mmol the contact angle start to increase somewhat. The surface tension is consistent, however over the range of concentration.

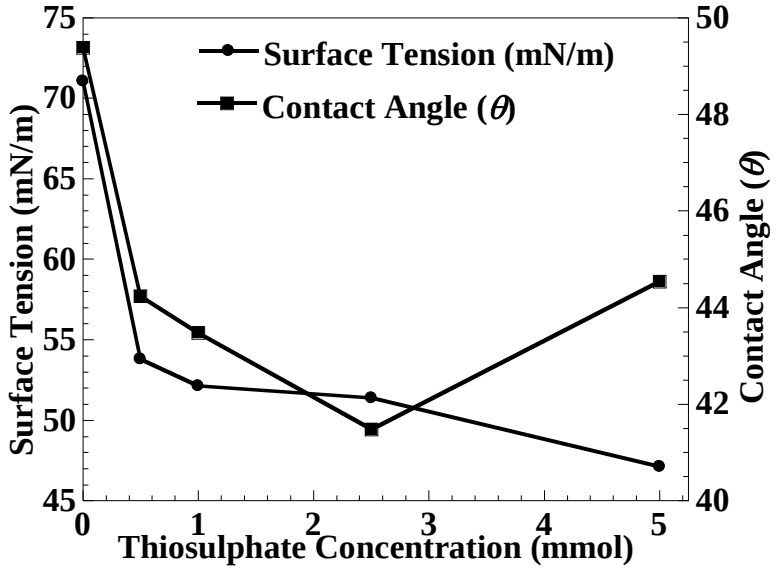

Figure 4.3 effect of thiosulphate concentration on surface tension and contact angle on glass surface.

In figure 4.4 shows the effect of TBOT concentration on surface tension and contact angle. Surface tension shows the same trend as that of thiosulphate concentration.

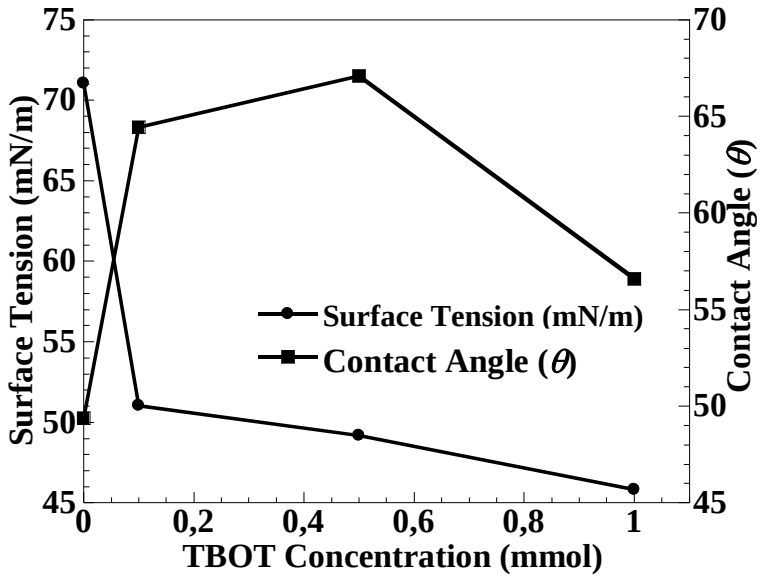

Figure 4.4 Effect of TBOT concentrations on surface tension and contact angle on glass surface.

At low concentration the values of surface tension is 71.2.mN/m and it start sharp decreases with increasing TBOT concentration until 0.15mmol concentration. Beyond this concentration there is a gradual decrease in the surface tension with increase in concentration.

But the effect of TBOT concentration on contact angle is different from what we observed in the figure 4.3.At low concentration it has a lowest value, say 49.5 (θ) and it started increasing with increase in concentration up to 0.5 mmol concentration. Beyond that it started decreases with increase in concentration. This result attributed to the effect of particles available in the solutions. It is well documented that particles available in a droplet are adsorbed to the surface. This interaction of the particle with the surface and their accumulation at the surface can hinder the penetration of the solution to the surface pores. Therefore, it is thermodynamically unfavourable for the particle solution to enter the surface pores and wetting would be kept in the composite mode. High contact angles, therefore, result for particle solution with the similar low surface tension when compared to pure liquids. In comparing the contact angles of particle with those of pure liquids it should be noted that the adsorption of the particles to the surface might change the solid surface energy and, hence, influence the observed contact angle to a limited degree.

4.2.2 Effect on the Teflon surface

The change in advancing contact angle and surface tension on the Teflon surface was studied and plotted in the figure 4.5.The figure shows that there is a gradual decrease in the surface tension with increasing thiosulphate concentration.

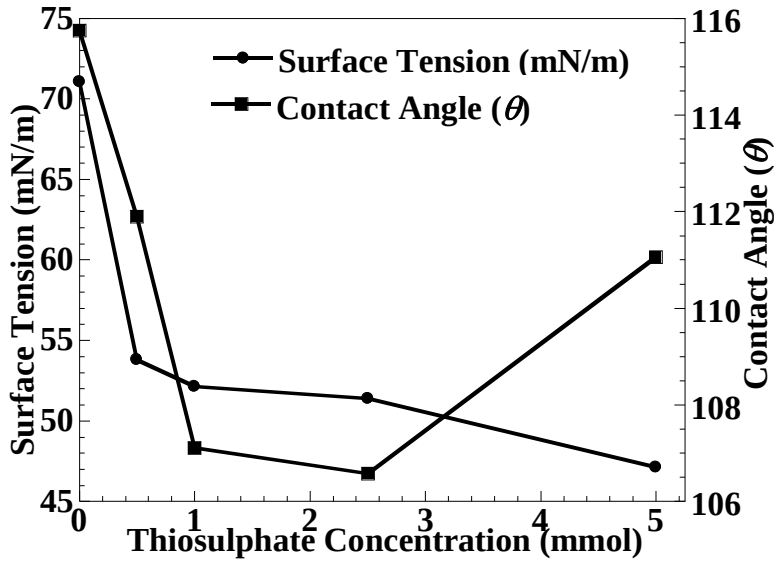

Figure 4.5 Effect of thiosulphate concentration on surface tension and contact angle on Teflon surface.

The theoretical concept is the energy minimization starting from Young's equation for ideal surface, $\cos\theta = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$ where θ is the contact angle and γ_{SV}, γ_{SL} and γ_{LV} are the solid –vapour (SV), liquid-solid (SL) and liquid-vapour (LV) surface energies, respectively. For reduction in contact angle, reduction in both the interfacial surface energy is important to enhance the wetting process. This effect is clearly shown in the figure 4.5.Thiosulphate concentration shows a remarkable increase in the contact angle beyond concentration 0.25 mmol/L.

Figure 4.6 shows the effect of TBOT concentration on surface tension and contact angle. The figure shows that there is a gradual decrease both in the surface tension and contact angle with increasing TBOT concentration. Beyond concentration 0.45mmol/L both remain constant in decreasing rate.

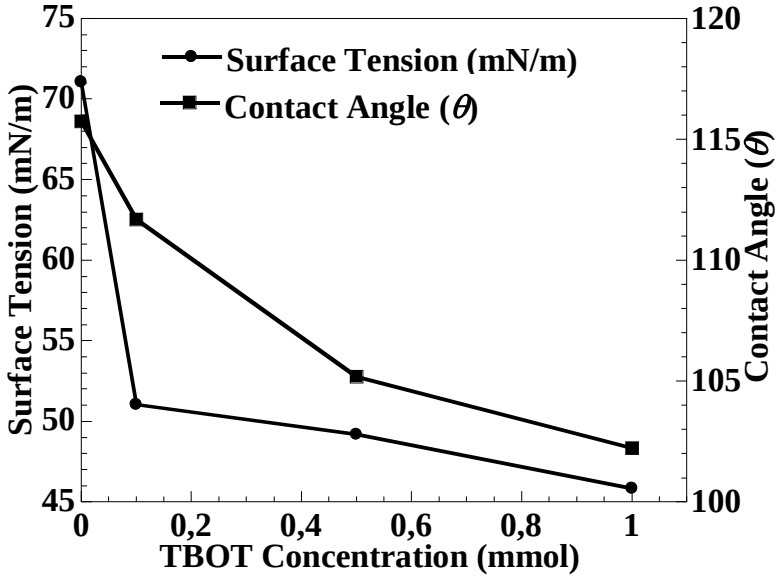

Figure 4.6 Effect of TBOT concentrations on surface tension and contact angle on Teflon surface.

4.3 Effect of the particles on work of adhesion, Hamaker constant, and wetting free energy

4.3.1 Effect on the glass surface

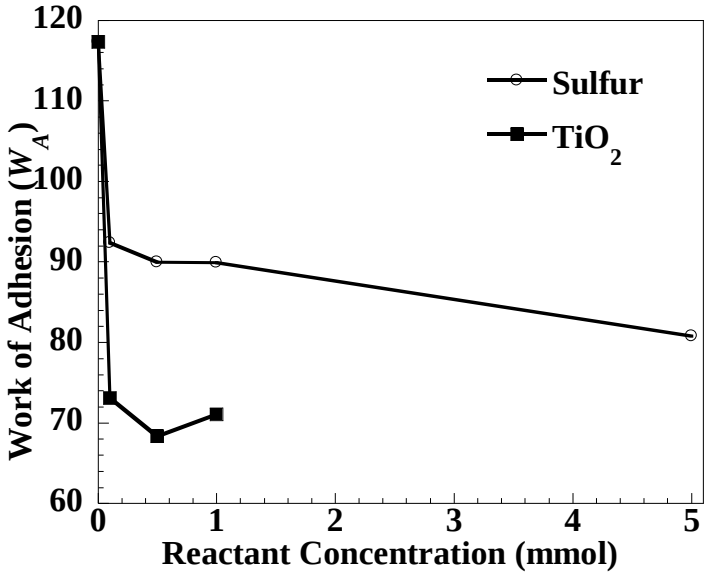

Figure 4.7 Effect of reactant concentration on work of adhesion (W_A) for sulfur and TiO_2 on glass surface.

Dependence between the work of adhesion and reactant concentration for sulfur and TiO_2 on the glass surface are shown in the figure 4.7.The solid-solution interfacial tension fulfill the condition

$$\gamma SL = \gamma SV + \gamma LV - W_A \quad (5)$$

Where W_A is the work of adhesion of liquid to solid surface. Using Young's equation another relation can be established as

$$W_A = \gamma SL(cos\theta + 1) \quad (6)$$

This equation implies that work of adhesion decreases a bit for TiO_2 with increase in concentration of the reactant, whereas for sulfur initially it shows a sharp decrease in the work of adhesion with increasing concentration up to 0.1 mmol concentration. Beyond 0.1mmol concentration one can find a gradual decrease in the work of adhesion (W_A).TiO_2 has lower value than sulfur throughout the studied.

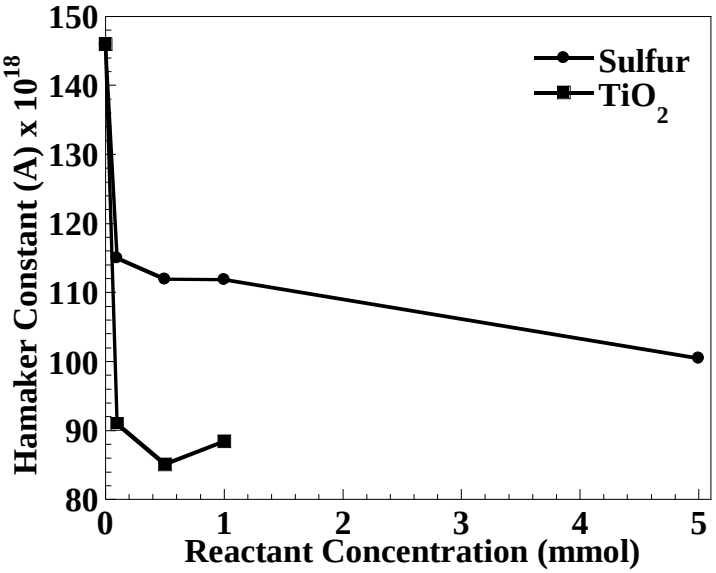

Figure 4.8 Effect of reactant concentration on Hamaker Constant (A) for sulfur and TiO_2 on glass surface

Hamaker constant is a key property in determining the wetting behavior and also in determining the spreading behavior .The dependency of the reactant concentration on

Hamaker constant (A) for sulfur and TiO_2 on the glass surface is plotted in the figure 4.8.Similarily to the plot for work of adhesion, at lower concentration, there are slight irregularity for both sulphur and TiO_2 and at higher concentration there is a decrease in Hamaker constant with increasing reactant concentration for sulfur. But it has a little effect on TiO_2 at higher concentration.

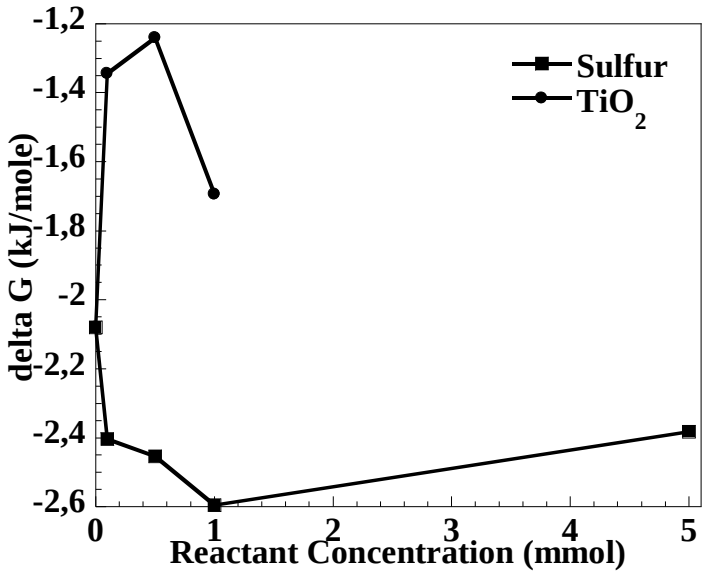

Figure 4.9 Effect of reactant concentration on wetting free energy (ΔG) for sulfur and TiO_2 on glass surface.

The clean glass surface has high surface free energy and the wetting ability of a liquid is a function of the surface energies of the solid-gas interface, liquid-gas interface and the solid-liquid interface. Figure 4.9 shows the dependency of wetting free energy (ΔG) on the reactant concentration for sulfur and TiO_2 on glass surface. As the sulfur has higher contact angle which indicate the lower surface energy as clearly shown in the figure 4.9.as compare to TiO_2.At lower concentration sulfur shows a slight irregularities up to 0.1mmol concentration and beyond this concentration it's increasing with increase in reactant concentration. TiO_2 shows a different trend at low concentration ,$\Delta G_{\text{for TiO2}}$ =-2 kJ/mole and with increase in concentration it becomes less negative and beyond 0.55 mmol concentration it becomes more and more negative which is important for enhancing the wetting process.

4.3.2 Effect on the Teflon surface

As the PTFE surface energy is low, wetting is difficult using only water with high surface energy~71.50 mN/m. In the presence of reactant solution, hydrophobic surfaces change to

hydrophilic by increasing the surface energy, as the particles are adsorb on the Teflon surface. Thus, knowledge of change in wetting free energy is also very important; as larger the values of the negative wetting free energy are expected to enhance the wetting process. According to Extrand, the molar wetting free energy of the solid can be calculated as follows.

$$\Delta G = \frac{RT}{3} [\ln (1 - \cos\theta)^2 (2 + \cos\theta)] / 4 \quad (7)$$

It is clear from the figure 4.10 that the wetting free energy becomes more negative with increase in reactant concentration for sulphur whereas it has less significant effect on TiO_2.

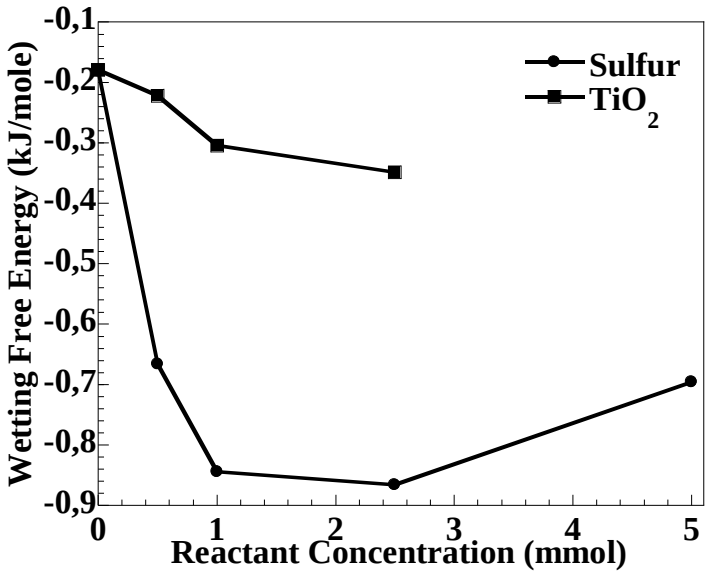

Figure 4.10. Change in the surface wetting free energy (kJ/mole) with concentration (mmol) for sulphur and TiO_2 on Teflon surface.

The work of adhesion measures the interactive force between the solid and liquid phases. These interactions between the phases and contact angle can be presented using the Dupree and Young-Dupree equations, respectively

$$W_A = \gamma_{LG} + \gamma_{SG} - \gamma_{SL} \quad (8)$$

$$W_A = \gamma_{LG} (1 + \cos\theta) \quad (9)$$

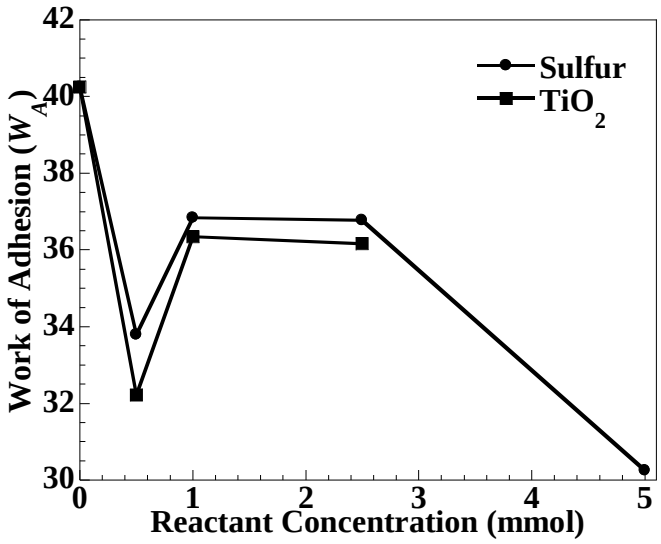

Figure 4.11 Effect of work of adhesion (W_A) on reactant concentrations for sulphur and TiO_2 on Teflon surface.

The work of adhesion depends on both the surface tension and contact angle; for zero contact angle, $W_A=2\gamma_{LG}$. Thus, zero contact angle results when liquid - solid attraction forces are equal to or greater than those between liquid- liquid attraction, and a finite contact angle results when the liquid adheres to the solid less than it coheres to itself. In the figure 4.11we plotted the values of work of adhesion at different concentration and its shows that with increasing reactant concentration the values of W_A decrease with a slight irregularity. TiO_2 has lower values than sulphur throughout the studied. The change in W_A can also be attributed to the unequal surface excesses between the air-liquid and solid-liquid interfaces.

Mathematically, it can be shown as follows using the differential form of above equation.

$$\frac{dWa}{d\gamma LG} = \frac{d\gamma SG}{d\gamma LG} - \frac{d\gamma SL}{d\gamma LG} + 1 \qquad (10)$$

From the Gibbs adsorption equation, $d\gamma_{SG}/d\gamma_{LG} = \Gamma_{SG}/\Gamma_{LG}$, and $d\gamma_{SL}/d\gamma_{LG} = \Gamma_{SL}/\Gamma_{LG}$. Assuming $\Gamma_{SG} \approx 0$ (equal surface excesses on the two interfaces) $\Gamma_{SL}/\Gamma_{LG} = 1$, and $dW_A/\gamma LG = 0$, or W_A = constant. Therefore, it can be assumed that the W_A will not change with reactant concentration. But as shown before, $\Gamma_{SL}/\Gamma_{LG} < 1$, or $dW_A/d\gamma_{LG} \neq 0$, which indicates that that the W_A will change with the reactant concentration. To further analyzing the results, it was observed that, although, in the presence of particle solutions contact angle decreases, the work of adhesion also decreases simultaneously. In general, from a basic understanding, decrease in contact angle enhances the wetting property; as a result, W_A

increases. This result can be attributed to the fact that, initially, in the presence of water and low reactant concentration, the contact angle on the PTFE surface is above 90°, where cos θ<0. As a result, contact angle decreases gradually with the (1+cos θ) term increases. At the same time, the surface tension also decreases gradually, which is greater than the increases in the (1+ cos θ) term; as a result, with increasing concentration the W_A values.

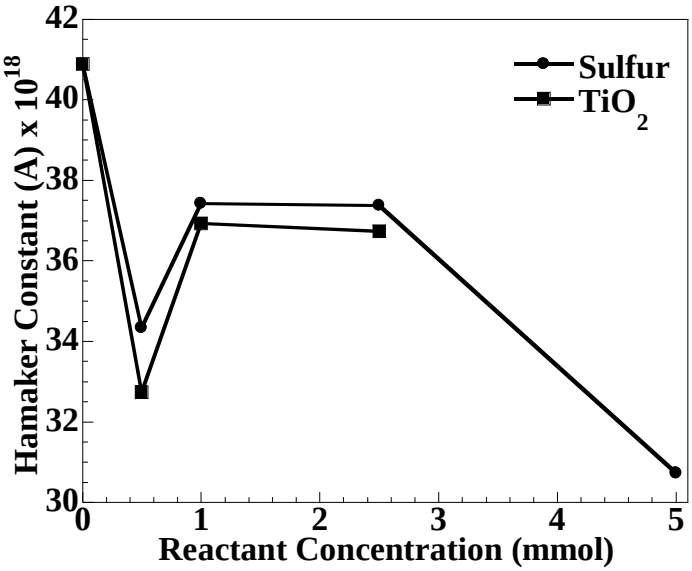

Figure 4.12 Effect of reactant concentration on Hamaker constant (A) for sulfur and TiO_2 on Teflon surface.

For discussion of the interaction between solid and liquid it is very important to determine the Hamarker constant (A) for a given material in the reactant solution. The Hamaker constant is positive (A > 0), it means the molecules are attracted toward each other, and when it is negative (A < 0), it corresponds to repulsion. Literature values of Hamaker constant in a vacuum for water and PTFE are $A_{water} = 3.8 \times 10^{-20}$ J and $A_{PTFE} = 4.4 \times 10^{-20}$J respectively. Similarly to the plot for the work of adhesion, there are slight irregularities at low reactant concentrations, but at higher concentrations, there is a sharp decrease in Hamaker constant with increasing concentration for sulphur, and it remains constant for TiO_2. Throughout the concentration range studied, TiO_2 exhibited lower values than sulphur.

Conclusion

An experimental study has been carried out on effect of nanoparticles (sulfur and TiO_2) on wetting of different solid surfaces. The effects of nanoparticles concentration concentration and particle size on work of adhesion, Hamaker constant and wetting free energy for both the surfaces in presence of both the particles are studied. The following conclusions are obtained:

- Addition of nanoparticles into the base liquid enhances the wetting property in case of sulfur nanoparticles for both the surfaces and the enhancement increases with increasing particle concentration and decreasing particle size.
- Addition of TiO_2 nanoparticle enhances the wetting property for PTFE surface but decreases for the glass surface. Reduction in contact angle is attributed to change in surface energy and surface tension by the presence of nanoparticles.
- Decrease in work of adhesion at low concentration and sharp decrease at high concentration (sulfur nanoparticle).
- TiO_2 exhibit lower Hamaker constant value than sulfur in both the surfaces.
- TiO_2 exhibit higher wetting free energy than sulfur for both surfaces.

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